

[47 FR 54912, Dec. 6, 1982; 48 FR 17355, Apr. 22, 1983]

APPENDIX C TO PART 50—MEASUREMENT PRINCIPLE AND CALIBRATION PROCEDURE FOR THE MEASUREMENT OF CARBON MONOXIDE IN THE ATMOSPHERE (NON-DISPERSIVE INFRARED PHOTOMETRY)

1.0 APPLICABILITY

1.1 This non-dispersive infrared photometry (NDIR) Federal Reference Method (FRM) provides measurements of the concentration of carbon monoxide (CO) in ambi-

ent air for determining compliance with the primary and secondary National Ambient Air Quality Standards (NAAQS) for CO as specified in \$50.8 of this chapter. The method is applicable to continuous sampling and measurement of ambient CO concentrations suitable for determining 1-hour or longer average measurements. The method may also provide measurements of shorter averaging times, subject to specific analyzer performance limitations. Additional CO monitoring quality assurance procedures and guidance

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are provided in part 58, appendix A, of this chapter and in reference 1 of this appendix C.

2.0 Measurement Principle

- 2.1 Measurements of CO in ambient air are based on automated measurement of the absorption of infrared radiation by CO in an ambient air sample drawn into an analyzer employing non-wavelength-dispersive, infrared photometry (NDIR method). Infrared energy from a source in the photometer is passed through a cell containing the air sample to be analyzed, and the quantitative absorption of energy by CO in the sample cell is measured by a suitable detector. The photometer is sensitized specifically to CO by employing CO gas in a filter cell in the optical path, which, when compared to a differential optical path without a CO filter cell, limits the measured absorption to one or more of the characteristic wavelengths at which CO strongly absorbs. However, to meet measurement performance requirements, various optical filters, reference cells, rotating gas filter cells, dual-beam configurations, moisture traps, or other means may also be used to further enhance sensitivity and stability of the photometer and to minimize potential measurement interference from water vapor, carbon dioxide (CO2), or other species. Also, various schemes may be used to provide a suitable zero reference for the photometer, and optional automatic compensation may be provided for the actual pressure and temperature of the air sample in the measurement cell. The measured infrared absorption, converted to a digital reading or an electrical output signal, indicates the measured CO concentration.
- 2.2 The measurement system is calibrated by referencing the analyzer's CO measurements to CO concentration standards traceable to a National Institute of Standards and Technology (NIST) primary standard for CO, as described in the associated calibration procedure specified in section 4 of this reference method.
- 2.3 An analyzer implementing this measurement principle will be considered a reference method only if it has been designated as a reference method in accordance with part 53 of this chapter.
- 2.4 Sampling considerations. The use of a particle filter in the sample inlet line of a CO FRM analyzer is optional and left to the discretion of the user unless such a filter is specified or recommended by the analyzer manufacturer in the analyzer's associated operation or instruction manual.

3.0 Interferences

3.1 The NDIR measurement principle is potentially susceptible to interference from water vapor and ${\rm CO}_2$, which have some infrared absorption at wavelengths in common with ${\rm CO}$ and normally exist in the atmos-

phere. Various instrumental techniques can be used to effectively minimize these interferences.

4.0 Calibration Procedures

- 4.1 Principle. Either of two methods may be selected for dynamic multipoint calibration of FRM CO analyzers, using test gases of accurately known CO concentrations obtained from one or more compressed gas cylinders certified as CO transfer standards:
- 4.1.1 Dilution *method*: A single certified standard cylinder of CO is quantitatively diluted as necessary with zero air to obtain the various calibration concentration standards needed
- 4.1.2 Multiple-*cylinder method*: Multiple, individually certified standard cylinders of CO are used for each of the various calibration concentration standards needed.
- 4.1.3 Additional information on calibration may be found in Section 12 of reference
- 4.2 Apparatus. The major components and typical configurations of the calibration systems for the two calibration methods are shown in Figures 1 and 2. Either system may be made up using common laboratory components, or it may be a commercially manufactured system. In either case, the principal components are as follows:
- 4.2.1 CO standard gas flow control and measurement devices (or a combined device) capable of regulating and maintaining the standard gas flow rate constant to within ± 2 percent and measuring the gas flow rate accurate to within ± 2 percent, properly calibrated to a NIST-traceable standard.
- 4.2.2 For the dilution method (Figure 1), dilution air flow control and measurement devices (or a combined device) capable of regulating and maintaining the air flow rate constant to within ± 2 percent and measuring the air flow rate accurate to within ± 2 percent, properly calibrated to a NIST-traceable standard.
- 4.2.3 Standard gas pressure regulator(s) for the standard CO cylinder(s), suitable for use with a high-pressure CO gas cylinder and having a non-reactive diaphragm and internal parts and a suitable delivery pressure.
- 4.2.4 Mixing chamber for the dilution method of an inert material and of proper design to provide thorough mixing of CO standard gas and diluent air streams.
- 4.2.5 Output sampling manifold, constructed of an inert material and of sufficient diameter to ensure an insignificant pressure drop at the analyzer connection. The system must have a vent designed to ensure nearly atmospheric pressure at the analyzer connection port and to prevent ambient air from entering the manifold.

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4.3 Reagents

4.3.1 CO gas concentration transfer standard(s) of CO in air, containing an appropriate concentration of CO suitable for the selected operating range of the analyzer under calibration and traceable to a NIST standard reference material (SRM). If the CO analyzer has significant sensitivity to CO₂, the CO standard(s) should also contain 350 to 400 ppm CO₂ to replicate the typical CO₂ concentration in ambient air. However, if the zero air dilution ratio used for the dilution method is not less than 100:1 and the zero air contains ambient levels of CO₂, then the CO standard may be contained in nitrogen and need not contain CO₂.

4.3.2 For the dilution method, clean zero air, free of contaminants that could cause a detectable response on or a change in sensitivity of the CO analyzer. The zero air should contain < 0.1 ppm CO.

4.4 Procedure Using the Dilution Method

4.4.1 Assemble or obtain a suitable dynamic dilution calibration system such as

the one shown schematically in Figure 1. Generally, all calibration gases including zero air must be introduced into the sample inlet of the analyzer. However, if the analyzer has special, approved zero and span inlets and automatic valves to specifically allow introduction of calibration standards at near atmospheric pressure, such inlets may be used for calibration in lieu of the sample inlet. For specific operating instructions, refer to the manufacturer's manual.

4.4.2 Ensure that there are no leaks in the calibration system and that all flowmeters are properly and accurately calibrated, under the conditions of use, if appropriate, against a reliable volume or flow rate standard such as a soap-bubble meter or wet-test meter traceable to a NIST standard. All volumetric flow rates should be corrected to the same temperature and pressure such as 298.15 K (25 °C) and 760 mm Hg (101 kPa), using a correction formula such as the following:

$$F_c = F_m \frac{298.15 \times P_m}{760(T_m + 273.15)} \quad (1)$$

Where:

 F_c = corrected flow rate (L/min at 25 °C and 760 mm Hg).

 F_m = measured flow rate (at temperature T_m and pressure P_m),

 P_m = measured pressure in mm Hg (absolute), and

 T_m = measured temperature in degrees Celsius.

4.4.3 Select the operating range of the CO analyzer to be calibrated. Connect the measurement signal output of the analyzer to an appropriate readout instrument to allow the analyzer's measurement output to be continuously monitored during the calibration. Where possible, this readout instrument should be the same one used to record routine monitoring data, or, at least, an instrument that is as closely representative of that system as feasible.

4.4.4 Connect the inlet of the CO analyzer to the output-sampling manifold of the calibration system.

4.4.5 Adjust the calibration system to deliver zero air to the output manifold. The total air flow must exceed the total demand of the analyzer(s) connected to the output manifold to ensure that no ambient air is pulled into the manifold vent. Allow the analyzer to sample zero air until a stable response is obtained. After the response has stabilized, adjust the analyzer zero reading.

4.4.6 Adjust the zero air flow rate and the CO gas flow rate from the standard CO cylinder to provide a diluted CO concentration of approximately 80 percent of the measurement upper range limit (URL) of the operating range of the analyzer. The total air flow rate must exceed the total demand of the analyzer(s) connected to the output manifold to ensure that no ambient air is pulled into the manifold vent. The exact CO concentration is calculated from:

$$[CO]_{OUT} = \frac{[CO]_{STD} \times F_{CO}}{F_D + F_{CO}} \quad (2)$$

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Where:

 $[CO]_{OUT}$ = diluted CO concentration at the output manifold (ppm),

[CO]_{STD} = concentration of the undiluted CO standard (ppm),

 F_{CO} = flow rate of the CO standard (L/min), and

 F_D = flow rate of the dilution air (L/min).

Sample this CO concentration until a stable response is obtained. Adjust the analyzer span control to obtain the desired analyzer response reading equivalent to the calculated standard concentration. If substantial adjustment of the analyzer span control is required, it may be necessary to recheck the zero and span adjustments by repeating steps 4.4.5 and 4.4.6. Record the CO concentration and the analyzer's final response.

4.4.7 Generate several additional concentrations (at least three evenly spaced points across the remaining scale are suggested to verify linearity) by decreasing F_{CO} or increasing F_D . Be sure the total flow exceeds the analyzer's total flow demand. For each concentration generated, calculate the exact CO concentration using equation (2). Record the concentration and the analyzer's stable response for each concentration. Plot the analyzer responses (vertical or y-axis) versus the corresponding CO concentrations (horizontal or x-axis). Calculate the linear regression slope and intercept of the calibration curve and verify that no point deviates from this line by more than 2 percent of the highest concentration tested.

4.5 Procedure *Using the Multiple-Cylinder Method*. Use the procedure for the dilution method with the following changes:

- 4.5.1 Use a multi-cylinder, dynamic calibration system such as the typical one shown in Figure 2.
- 4.5.2 The flowmeter need not be accurately calibrated, provided the flow in the output manifold can be verified to exceed the analyzer's flow demand.
- 4.5.3 The various CO calibration concentrations required in Steps 4.4.5, 4.4.6, and 4.4.7 are obtained without dilution by selecting zero air or the appropriate certified standard cylinder.
- 4.6 Frequency of Calibration. The frequency of calibration, as well as the number of points necessary to establish the calibration curve and the frequency of other performance checking, will vary by analyzer. However, the minimum frequency, acceptance criteria, and subsequent actions are specified in reference 1, appendix D, "Measurement Quality Objectives and Validation Template for CO" (page 5 of 30). The user's quality control program should provide guidelines for initial establishment of these variables and for subsequent alteration as operational experience is accumulated. Manufacturers of CO analyzers should include in their instruction/operation manuals information and guidance as to these variables and on other matters of operation, calibration, routine maintenance, and quality con-

5.0 Reference

1. QA Handbook for Air Pollution Measurement Systems—Volume II. Ambient Air Quality Monitoring Program. U.S. EPA. EPA-454/B-08-003 (2008).

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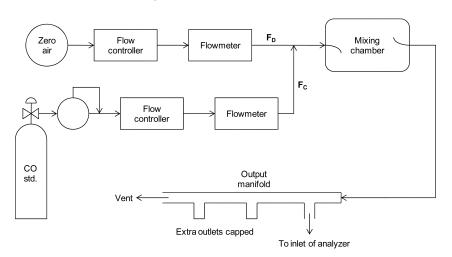


Figure 1. Dilution method for calibration of CO analyzers.

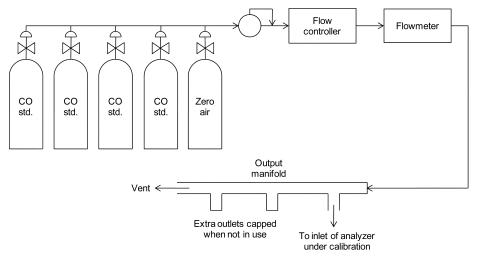


Figure 2. Multiple cylinder method for calibration of CO analyzers.

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